

Time-dependent Nonlinear Optical Susceptibility of an Out-of-Equilibrium Soft Material

Neda Ghofraniha¹, Claudio Conti², Giancarlo Ruocco^{1,2} and Francesco Zamponi³

¹*Dipartimento di Fisica, Universita' di Roma "La Sapienza", P. A. Moro 2, 00185, Roma, Italy*

²*SOFT-INFM-CNR, c/o Universita' di Roma "La Sapienza", P. A. Moro 2, 00185, Roma, Italy*

³*Laboratoire de Physique Théorique, École Normale Supérieure,*

24 Rue Lhomond, 75231 Paris Cedex 05, France

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We investigate the time-dependent nonlinear optical absorption of a clay dispersion (Laponite) in organic dye (Rhodamine B) water solution displaying liquid-arrested state transition. Specifically, we determine the characteristic time τ_D of the nonlinear susceptibility build-up due as to the Soret effect. By comparing τ_D with the relaxation time provided by standard dynamic light scattering measurements we report on the decoupling of the two collective diffusion times at the two very different length scales during the aging of the out-of-equilibrium system. With this demonstration experiment we also show the potentiality of nonlinear optics measurements in the study of the late stage of arrest in soft materials.

Light can influence matter microscopic properties providing an optical response that depends on the laser power. The nonlinear optical susceptibility of a wide variety of materials (e.g. simple liquids [1], magnetic fluids [2, 3], liquid crystals [4], polymeric thin films [5] and nano-composite layers [6]) has been investigated by using different techniques. Time-resolved Z-scan [7] has been used to distinguish between different nonlinear effects in crystals and in liquids and transient holographic gratings [8] allowed to study the thermal diffusion of nanospheres. Nonlinear optics in soft material has been explored in diluted colloidal suspensions [9], in metallic nanoparticles [10] with different chemical stabilizers [11], in presence of nanoparticles aggregation [12] and recently in out-of-equilibrium systems [13, 14].

Complex fluids far from thermodynamic equilibrium are known to display *aging* [15, 16], meaning that dynamical quantities such as correlations and responses depend on the time spent since the sample preparation (*waiting time* t_w). The same is expected for the dynamics of nonlinear optical self-action effects, like self-phase modulation and nonlinear absorption, an issue that so far remains unexplored. These effects can be used to determine the Soret coefficient and the collective diffusion coefficient of the colloidal particles moving on length scales much larger than particles size. Therefore the presented nonlinear optics experiments can be very useful to characterize dynamical properties of colloidal systems, for instance *i)* to study the dynamics of jammed systems characterized by long range interactions and *ii)* to analyze the dynamical properties of weakly turbid samples, not detectable by standard light scattering measurements.

In this Letter we report on the time-dependent optical nonlinearity of a complex out-of-equilibrium system during

its dynamics slowing down. The investigated soft-medium is a dye-doped clay (Laponite) dispersed in water. The suspension is prepared by solving the Laponite powder, supplied by Laporte Ltd., in a solution of Rhodamine-B (RhB) and deionized water at 0.1 mM concentration. The suspension at 1.6 wt% clay concentration is then stirred vigorously until it is cleared and filtered through 0.22 μm pore size Millipore filter. The sample is prepared in air and we take the time when the suspension is filtered as the starting aging time ($t_w = 0$). Once dispersed in water Laponite platelets start to aggregate and their dynamics slows down leading to a liquid-arrested state transition [17]. In the mentioned RhB-water-Laponite suspension all dye molecules attach to the clay particles surface [18]. We estimate about 10 dye molecules per platelet, much less than the maximum allowed adsorption sites (about 500 as provided by Laporte Ltd. data-sheet). The RhB molecules absorb visible light that locally heats up the medium and the induced thermal gradient influences both water density and dielectric properties (thermal effect) [19] and colloidal particle concentration (thermo-diffusive or Soret effect) [20]. Both phenomena lead to a nonlinear optical response characterized by distinct time scales: $\sim ms$ and $\sim s$, respectively. The thermal effect is responsible of local refraction changes (thermal lens), while the Soret effect in principle can produce either absorption or refraction variations. To study this twofold effect we perform both non-linear refraction and absorption measurements.

By using the Z-scan approach, for refraction experiments the light source is a CW pumped diode laser operating at wavelength $\lambda = 532\text{ nm}$ modulated by a mechanical shutter with opening time $700\mu\text{s}$. The beam is focused by a 75 mm focal-length lens providing a 35 μm beam waist radius w at the sample position. A photo-detector with rise-time 14 ns and an angular acceptance of 0.73° was used to probe the light power. Being the beam spot on the detector larger than the photo-diode surface, only the light transmitted along the beam axis is collected, giving access to the nonlinear phase shift [21]. For absorption experiments we use the same setup in addition with a 25 mm focal-length lens before the detector, thus collecting the whole transmitted beam. The colloidal dispersion is syringed in a glass cuvette with transverse dimensions $10 \times 35\text{ mm}^2$ and 1 mm thickness along the beam axis. Each single measurement is the response of a different point of the sample not previously illuminated. We investigate the doped clay response at four different incident laser powers for each t_w , during which we consider unchanged the dynamics and structural properties of Laponite at 1.6% w/w, as inferred from Dynamic Light Scattering (DLS) measurements on the same sample.

Refraction measurements are aimed to distinguish between thermal and Soret time-scales. In Fig. 1 the normalized transmitted light intensity is reported displaying the two distinct times. The intensity is normalized such that its value gives $\Delta\bar{n}(t)/\Delta\bar{n}_T$, where $\Delta\bar{n}(t)$ is the nonlinear phase shift per unit length and unit intensity (radial integral of the bell shaped $\Delta\bar{n}(r, t)$, with r the transversal radial coordinate) and $\Delta\bar{n}_T$ corresponds to the saturation of the thermal contribution. At short times the temperature gradient induces mostly water density variation, which provides a change of the index of refraction $\Delta n(t) < 0$ (thermal lens) that broadens the input beam. Being the sample positioned before the focus of the lens ($z=0$, as shown in the inset of 1), the transmitted beam gets narrower augmenting the detected light intensity. In Fig. 1 the intensity growth at large times is due to the dyed clay thermal-diffusion, that induces

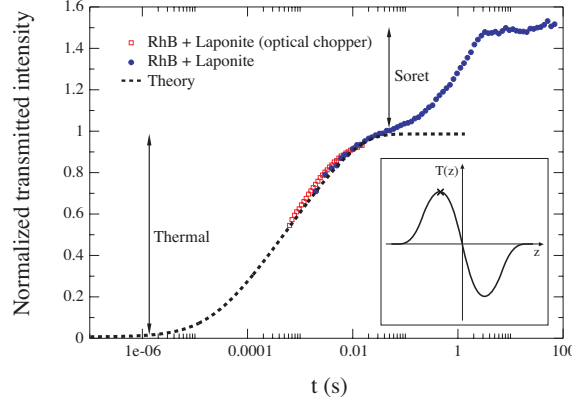


FIG. 1: **Refraction.** Normalized transmitted light intensity of 0.1mM RhB-water+1.6% w/w Laponite dispersion compared to the theoretical thermal lens curve (solid line)- see text. Input power 8.3 mW. Inset: sketch of z-scan profile; the cross corresponds to the sample position.

variation of light absorption influencing the refractivity. Z-scans experiments [14] show that the RhB-platelets diffusion drastically alters the nonlinear absorption that is considered with details in the following. In Fig. 1, at short times, the thermal effect is compared to the theoretical curve from [22], calculated with our experimental parameters. From the comparison we have $t^* = 65 \text{ ms}$ as the time when the thermal gradient can be regarded as stationary.

In the following nonlinear optical absorption and its evolution during the gelation of the soft material is considered. The transmitted intensity is $I(r, t) = I_0(r) \exp[-\alpha(r, t) L]$ with $I_0(r) = I_0 \exp(-2r^2/w^2)$ the input, w the beam waist, I_0 the peak value and L the sample thickness. The absorption coefficient $\alpha(r, t) = \alpha_0 + \Delta\alpha[I(r, t)]$ can be written as the sum of a constant term (the linear absorption coefficient) and a time and laser intensity dependent term $\Delta\alpha[I(r, t)]$ that is related to the gradient of particles mass fraction $\Delta c[I(r, t)]$ by

$$\Delta\alpha[I(r, t)] = \left(\frac{\partial \alpha}{\partial c} \right)_{\bar{c}} \Delta c[I(r, t)], \quad (1)$$

where \bar{c} is the average mass fraction. $\Delta\alpha[I(r, t)]$ is the response of the out-of-equilibrium system to the solicitation $I(r, t)$, which is proportional to the local temperature gradient responsible of the platelets diffusion. We consider the series expansion of $\Delta\alpha[I(r, t)]$ in terms of I_0 : the first term is the susceptibility linear in the perturbation and it can be described by the linear hydrodynamics equations [equations (2) and (3) below]. The nonlinear absorption coefficient $\Delta\alpha[I(r, t)]$ can be obtained in our experiments by writing $\Delta\alpha(r, t) = -[I(r, t) - I(r, t^*)]/L I(r, t^*)$, where t^* is the starting time of the colloid Soret effect, $I(r, t^*) = I_0(r) \exp[-\alpha(r, t^*) L]$ and we retain the first term in the expansion $\exp[-\Delta\alpha(r, t) L]$. In this way we examine the contribution to the nonlinear optical susceptibility $\Delta\alpha(t)$, that is only due to platelets motion and hence its dependence on the structural properties of the jelling system. In the following we scale down the response function $\Delta\alpha(r, t)$ to the input power P_0 as $\Delta\alpha(r, t)/P_0$. In Fig. 2 we show the output signal $S(t) = -\langle \Delta\alpha(r, t) \rangle_r / P_0$ at four powers and two different aging times ($\langle \Delta\alpha(r, t) \rangle_r = \int_0^\infty dr r e^{-\frac{2r^2}{w^2}} \Delta\alpha(r, t) / \int_0^\infty dr r e^{-\frac{2r^2}{w^2}}$ is

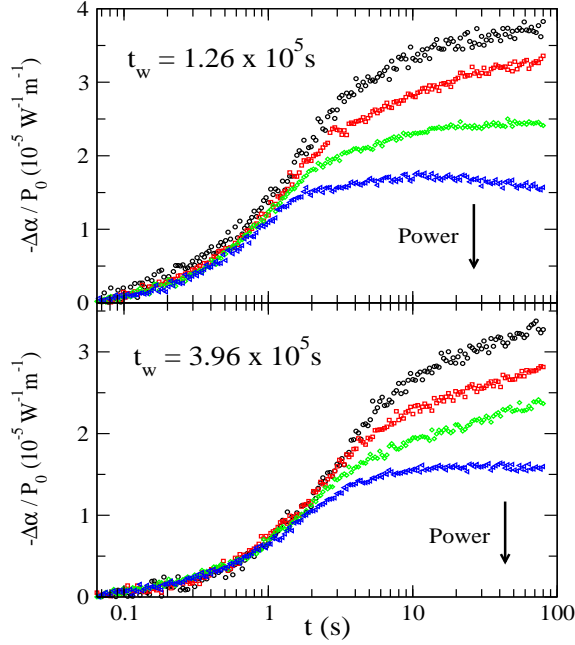


FIG. 2: **Absorption.** Scaled absorption coefficient of 0.1mM RhB-water+1.6% w/w Laponite dispersion at two different aging times. The four inject power values are: 8.3 mW, 11 mW, 14 mW and 17.8 mW.

the radial average over the incident intensity profile). In the range $65\text{ ms} < t < 1\text{ s}$ the signals at different input powers collapse on one curve defining the linear response regime. For $t > 1\text{ s}$ higher orders terms are relevant; these terms give direct access to the dynamical heterogeneity length scales [23] and their characterization will be reported elsewhere.

In the “linear” regime ($65\text{ ms} < t < 1\text{ s}$) the induced particle mass fraction change $\Delta c[I(r, t)]$ is given by the solution of the heat-mass flux coupled equations [24]

$$\begin{aligned} \frac{\partial}{\partial t} \Delta T(r, t) &= D_T \nabla^2 \Delta T(r, t) \\ &+ \frac{D_T D_D \bar{T} \mu_c}{k} \nabla^2 \Delta c(r, t) + \frac{D_T \alpha_0}{k} I(r) \end{aligned} \quad (2)$$

$$\begin{aligned} \frac{\partial}{\partial t} \Delta c(r, t) &= D_c \nabla^2 \Delta c(r, t) \\ &+ D_c S_T \bar{c} (1 - \bar{c}) \nabla^2 \Delta T(r, t) \end{aligned} \quad (3)$$

where $\Delta T(r, t)$ is the radial temperature variation due to the local light absorption, D_T and k are water thermal diffusivity and conductivity respectively, \bar{T} is the bulk temperature μ_c is the the variation of colloid’s chemical potential in presence of a concentration gradient and D_D is the Dufour coefficient; D_c is the particles collective diffusion coefficient and S_T is the Soret coefficient. As shown in Fig. 1 clay concentration gradient builds up once the temperature profile reaches a stationary state, this allows to neglect the Dufour effect in the heat equation and to take $\nabla^2 \Delta T(r, t)$ in (3) from the stationary solution of (2). In decoupling the two effects we consider negligible

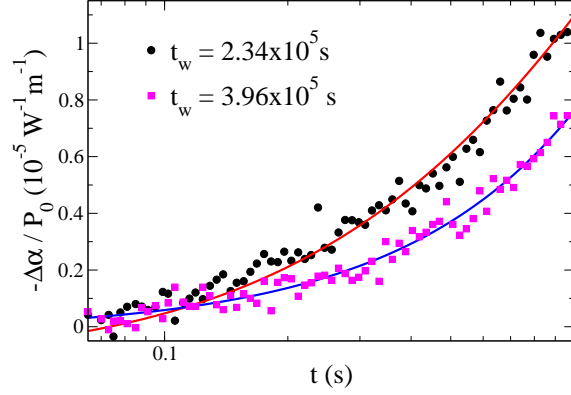


FIG. 3: **Absorption.** Scaled absorption coefficient of 0.1mM RhB-water+1.6% w/w Laponite dispersion and the fitting curves (full lines) by using expression (5).

the Soret feedback on the temperature profile, being $(|\alpha_2| I_0)/\alpha_0 \sim 10^{-5}$, where the coefficients $\alpha_0 = 0.86 \text{ mm}^{-1}$ and $\alpha_2 = -2.8 \text{ nm/W}$ are obtained by fitting $\log[I_0/I(t = 1\text{s})] = L(\alpha_0 + \alpha_2 I_0)$ vs. I_0 . In this approximation the colloidal mass fraction variation leads to

$$\Delta c(r, t) = \frac{\bar{c} S_T \alpha_0 P_0}{4\pi k} \left[Ei\left(-\frac{2r^2}{w^2}\right) - Ei\left(-\frac{2r^2}{w^2} \frac{1}{1 + 2t/\tau_D}\right) \right], \quad (4)$$

being $P_0 = I_0 \pi w^2$ the beam power, $\tau_D = w^2/4D_c$ the characteristic diffusion time over the beam spot size, and Ei the exponential integral function. To analyze the observed nonlinear absorption in our experiments by means of equation (4) we consider the output signal

$$\begin{aligned} S(t) &= -\langle \Delta \alpha(r, t) \rangle_r / P_0 \\ &= L\left(\frac{\partial \alpha}{\partial c}\right)_{\bar{c}} \frac{\bar{c} S_T \alpha_0}{4\pi k} \log\left(1 + \frac{t}{\tau_D}\right) \end{aligned} \quad (5)$$

as obtained by using expressions (1) and (4). We use equation (5) to fit the experimental results at different t_w values. We show in Fig. 3 the output data with the fitting curves (solid lines) at two aging times and in Fig. 4-a the fitted characteristic thermo-diffusion times τ_D at various t_w . We find that this characteristic time exponentially grows during aging as the structural relaxation time $\tau_M(t_w)$ obtained from DLS measurements, which are contemporarily performed on the same sample. DLS data were fitted assuming a correlation function made by square of the sum of an exponential function with relaxation time τ_1 and a stretched exponential function with relaxation time τ_2 and stretching coefficient β . The mean relaxation time is defined as $\tau_M = \tau_2 \beta^{-1} \Gamma(\beta^{-1})$ with $\Gamma(x)$ the usual Euler gamma function. Indeed we fit both $\tau_D(t_w)$ and the mean relaxation time $\tau_M(t_w)$ (representing the slow dynamics of the correlation function) with the exponential growth law $\tau = \tau_0 + \tau_1 \exp(\mu t_w)$ (full lines trough data) as shown in Fig. 4-a and Fig. 4-b respectively. Both τ_D and τ_M describe the collective diffusion of interacting particles on different

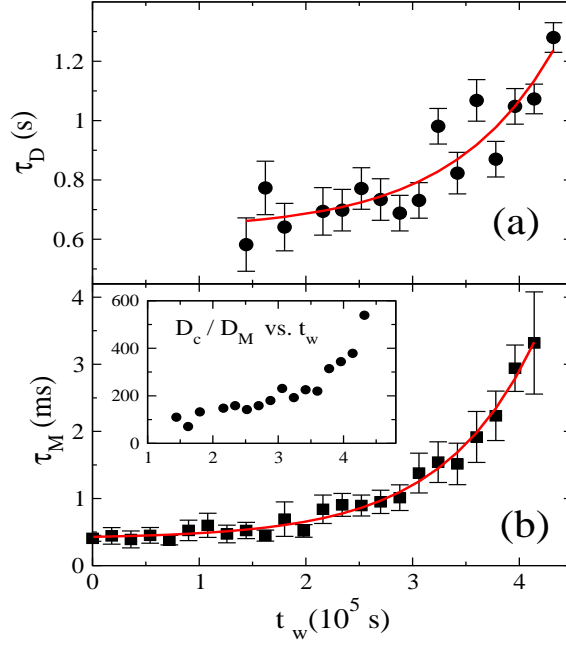


FIG. 4: Characteristic thermo-diffusion time (a) and mean relaxation time (b) vs. t_w and the fitting exponential curves (full lines). Inset: the ratio D_c/D_M vs. t_w

length scales: DLS probes dynamics on $1/q \simeq 50$ nm and nonlinear susceptibility on $w \simeq 35$ μ m. Although we find comparable growth rates μ from the fitting procedure, the ratio D_c/D_M [with $D_c = w^2/(4\tau_D)$ and $D_M = 1/(q^2\tau_M)$] reported in the inset of 4-b as a function of t_w increases of approximately one order of magnitude in the accessible waiting-time window. Moreover at very low t_w the two diffusion coefficients are not the same. This behavior can be attributed to the long ranged (screened electrostatic) interactions between Laponite particles, characterized by the peculiarity of non-homogeneous surface charge distribution, that makes the system strongly interacting on relatively large length scales even at very small t_w [25]. Another possible explanation might be the deviation to the Fluctuation-Dissipation Relation (FDR) in an out-of-equilibrium glassy system [15]. Indeed the diffusion constant measured in optical absorption is related to the response of density to an external field, while the one measured in DLS is related to the correlation of density fluctuations. The mentioned discrepancy could be also related to a supradiffusive regime as shown in [26].

We finally estimate the Soret coefficient as $S_T \simeq 0.02$ K $^{-1}$ from the amplitude of the fitting expression (5), by considering $(\frac{\partial \alpha}{\partial c})_{\bar{c}} \simeq \alpha_0/\bar{c}$, and by using water thermal conductivity $k = 0.58$ W/m K. Notably enough the Soret coefficient, defined as $S_T = -(1/\bar{c}) d[\Delta c(t_w)]/dT$, is constant during the aging process and $S_T > 0$ thus indicating that the platelets migrate from hot to cold regions being $d(\Delta c(t_w))/dT < 0$.

In conclusion we measured the time-dependent nonlinear optical susceptibility of a soft-material evolving toward structural arrest. We characterized the dynamics of the nonlinear absorption in terms of material parameters as the characteristic diffusion time τ_D and the Soret coefficient. We have evidence of decoupling of two different diffusion

times probed on two distinct length scales signaling the existence of long ranged interactions between the colloidal particles and suggesting the violation of the FDR [27]. The nonlinear optical response can be hence used to investigate dynamical properties of colloidal gels characterized by long range interactions, especially the presented method can cover length ranges much larger than particles size, not detectable by scattering measurements; moreover it can be really useful in analyzing the dynamics of weakly turbid samples, not easily investigated by standard light scattering techniques.

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